

## CHAPTER II

### LITERATURE REVIEW

Since the Ziegler-Natta catalyst was applied to propylene polymerization [3,4], the problem about the production of isospecific polymer has become widely interested. They have tried approaches to this problem such as preforming of  $TiCl_3$  crystal structure [3]. Most of the researches were about the use of the electron donors as the third component in polymerization reaction [17,18,24-30,33]. This thesis will further examine various issues relating to this area of study. Due to a wide spectrum of the Ziegler-Natta catalyst, it was very difficult to handle a summarization of all investigations here. Survey of the literature in this review will limit to the brief history of Ziegler-Natta catalyst, the use of support and the research about the effect of an electron donor to improve stereospecificity of Ziegler-Natta catalyst in propylene polymerization.

In 1953 Ziegler [1,2] found the method to obtain linear polyethylene by using a combination of triethylaluminum and titanium tetrachloride. A year later, Natta [3,4] succeeded in using the same type of catalyst to prepare polypropylene. These catalysts were then later named Ziegler-Natta catalyst. These discoveries provoked a worldwide research and development effort that culminated in many new commercial plastics and elastomers.

In 1955 Vandenberg at Hercules [5] and Ettore and Luciano at Montecatini [6] applied for patents which disclosed that molecular hydrogen acted as a true transfer agent for the Ziegler-Natta catalysts. This was a very important discovery because many of the Ziegler-Natta catalysts produced polymers with molecular weights too high for facile processing and certain product applications. The desired molecular weight was easily obtained in the presence of hydrogen.

The use of supports in the heterogeneous catalysis was well understood by 1950 and was highlighted by the discovery in 1958 by Hogan and Banks [7] of highly active chromium trioxide catalysts supported on silica which could polymerize ethylene under mild conditions of temperature and pressure to produce predominantly linear, high density polyethylene. At about the same time Natta and co-workers [8] demonstrated that only a small percentage of the titanium atoms (<1%mol) in first generation  $\alpha$ -TiCl<sub>3</sub> / AlEt<sub>2</sub>Cl catalysts was active. It was evident that higher catalyst activities were likely to be achieved through the use of transition metal compounds supported on appropriate matrices. Over the years a wide range of supported catalysts have been successfully developed and used for the commercial production of polyethylene polypropylene.

A series of attempts were made to support the TiCl<sub>4</sub> on different carrier materials. Early attempts were made with the classical large-surface supports used in heterogeneous catalysis, i.e. SiO<sub>2</sub> [9] or MgCl<sub>2</sub> [10]. However, no

significant success was obtained along these until "Activated  $\text{MgCl}_2$ " was used as support [11-14].

Many hundreds of related catalysts had been claimed in the patent literature for ethylene, propylene and other  $\alpha$ -alkene polymerization. "Activated"  $\text{MgCl}_2$ , a key ingredient of these catalyst systems, had been known for some time, being mentioned by Bryce-Smith [15] in 1959, and described by Kaminski [16] in 1967. A number of preparation methods are available and include; (i) treatment of  $\text{MgCl}_2$  with activating agents such as electron donors; (ii) ballmilling  $\text{MgCl}_2$ ; and (iii) reaction of compounds such Grignard reagents with chlorinating agents. All three procedures had been found useful in catalyst preparation for olefin polymerization.

Some of the most promising catalysts, especially for propylene polymerization, have resulted from the use of magnesium chloride as supports. An early patent in 1960 described the use of ground  $\text{MgCl}_2$  with electron donors in propylene polymerization. However, it was the discoveries by Montecatini-Edison Co. [17] and Mitsui Petrochemicals Ind. [18] that catalysts, prepared from  $\text{MgCl}_2$ ,  $\text{TiCl}_4$  and electron donors and activated by a mixture of trialkylaluminum and an electron donor, could polymerize propylene with a high yield [ $>50\text{kg PP}(\text{g Ti})^{-1}$ ] and with good stereospecificity (isotactic index which is a fraction of

insoluble polymer in boiling heptane >90%), that have set the scene for much of the present explosion in catalyst development.

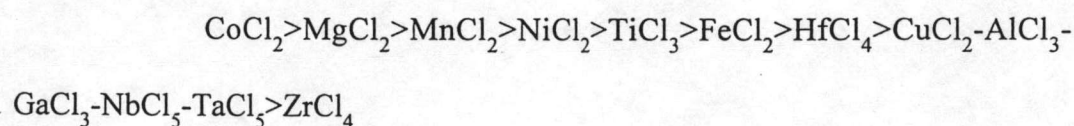
Boor [19] investigated the effect of the addition of compound containing lone-pair electrons to a given catalyst on isotacticity, polymerization rate, and molecular weight. Additions of  $\text{Et}_3\text{N}$  to a  $\text{ZnEt}_2\text{-TiCl}_3$ -based increase propylene polymerization activity. At the same time the isotacticity of the polymer increased. The author claimed that there exist isolated reaction sites on the surface of the  $\text{TiCl}_3$  crystals which show different capacities to coordinate electron donor compounds such as amines and olefins. Only exposed titaniums along the edges of the crystals favored stereospecific growth. The sites that are complexed most readily during the initial addition of amine had the fewest steric requirements. When they were complexed with amines they were dead and the net steric purity of the polymer rised while the overall activity of the catalysts fell.

A maximum value for the dependence of the catalyst activity on Al/Ti ratio was found by Schnecko et al. [20] employing an  $\text{AlEt}_3\text{-TiCl}_4$  catalyst system. The catalyst activity was expressed by the volume of ethylene consumed in one hour. The Al/Ti ratio at which the maximum activity occurred decreased as the polymerization temperature was increased. Another alkylating agent, ethylaluminum dichloride, was investigated to show no maximum resulting from

no reduction of titanium beyond its trivalent state and the same type of the resulting curve as obtained by direct use of  $\text{TiCl}_3$ . This result strongly indicated that the lower activity was caused by the reduction of the titanium beyond its optimum valence state at higher Al/Ti ratios, and this effect was emphasized at higher reaction temperatures.

Boucher et al. [21] investigated the polymerization of ethylene using magnesium reduced titanium trichloride catalysts together with the usual aluminum alkyl activator. The activity constant of this type of catalyst was reported at  $50^\circ\text{C}$  and 1 atm pressure a value of  $3.4 \times 10^6 \text{ g dm}^3 (\text{mol TiCl}_3)^{-1} \text{ h}^{-1}$  that  $10^{-2}$  times larger than for a conventional aluminium reduced  $\text{TiCl}_3$ . On the other hand the viscosity-molecular weight-time (or conversion) relation are not very different from those given by conventional catalysts. Analysis of the result suggested that a high portion (e.g 50%) of the titanium atoms in the magnesium reduced  $\text{TiCl}_3$  played as active sites.

Doi [22] studied the influence of metal chloride supports on polymerization activity in the polymerization of propylene with the soluble  $\text{Ti}(\text{OC}_4\text{H}_9)_4/\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}/\text{MCl}_x$  catalyst system. The polymerization activity was in the order :



A clear relation was found between the polymerization activity and the electronegativity of the metal ion in the metal chloride.

Floyd et al. [23] studied the polymerization rate behavior of the growing polymer of ethylene and propylene in slurry process. The degree of mass transfer limitation in Ziegler-Natta system was dependent on both the catalyst particle size and the size of primary crystallites. The significant concentration gradients in the macroparticles existed at short time in slurry polymerization, even for catalysts of relatively low activity. For large particles of high activity catalyst, intraparticle mass transfer resistance could be rate limiting over longer periods. The rate limitation resulted from mass transfer of both cocatalyst and monomer.

Chien and Hu [24] studied the functions of external lewis base, methyl-p-toluate, MPT for catalyst system,  $\text{MgCl}_2/\text{EB}/\text{PC}/\text{AlEt}_3/\text{TiCl}_4 - \text{AlEt}_3/\text{MPT}$  (EB was ethylbenzoate and PC was p-cresol). They found that the action of external lewis base was highly stereospecific. The isotacticity index of polypropylene was >95% in the presence of external electron donor but <68% without it.

Sacchi and co-workers [25] studied the effect of  $\text{Et}_3\text{N}$  and 2,2,6,6-tetramethyl-piperidine (TMPip) as donor additive on the catalyst  $\text{MgCl}_2/\text{TiCl}_4/\text{AlEt}_3$ ,  $\delta\text{-TiCl}_3/\text{AlEt}_3$  and  $\delta\text{-TiCl}_3/\text{ZnEt}_2$  for propylene polymerization. They found that amines exerted at least two different and

concurrent effects (i) poisoning of both the isotactic and the atactic sites ; (ii) activation of isotactic sites.

The former effect is due to the interaction between the uncomplexed base and activesites on the heterogeneous catalytic surface, the selective of the process depending on the steric hindrance of the base. The latter effect is connected with the presence in solution of the sufficient base-alkyl metal complex. Also the extent of the activation depend on the structure fo the base.

Kashiwa, Yoshitake and Toyota [26] performed polypropylene with highly active  $MgCl_2$  supported  $TiCl_4$  in conjunction with  $Et_3Al$  and ethylbenzoate (EB). The obtained polypropylene sample was separated into four fractions by successive extraction with pentane, heptane and trichloroethylene(trichlene). Yield,  $M_n$ ,  $T_m$  and microtacticity of each fraction were determined, and the effects of the concentration of EB on these items of results were investigated. It has been found that EB enhances yield,  $M_n$  and stereospecificity of trichlene insoluble ( the most stereospecific) fraction, and in contrast, it decreases rapidly yields of other three fractions without changing the character of the polymers.

Sugano [27] has found that the electron donor compound, diphenyl dimethoxymethane (DPDMM), is useful for the stereospecific polymerization of propylene. He studied the kinetic reaction of DPDMM with alkylaluminum. The

reaction atmosphere influence on the reaction rate and the reaction products. The stereospecificity of polypropylene depends on the concentration of DPDMM .

Terano [28] applied t.g.-d.t.a. (thermalgravimetry differential thermal analysis) in combination with infra-red (i.r.) spectroscopy to study the state of EB and  $\text{TiCl}_4$  in  $\text{MgCl}_2$ -supported catalyst for propylene polymerization, and found that :

(i)  $\text{TiCl}_4$ -EB complex decomposes by grinding with  $\text{MgCl}_2$ , on which  $\text{TiCl}_4$  and EB are supported independently.

(ii)  $\text{TiCl}_4$  directly coordinated by EB can barely form active sites.

(iii) increase of activity with grinding time is caused by an increase in active sites.

Seppälä and Härkönen [29] used nineteen silane compounds of the structure  $\text{R}_n\text{Si}(\text{OR}')_{4-n}$ , where  $n = 1-4$ ,  $\text{R} = \text{C}_6\text{H}_5$ , alkyl or H :  $\text{R}' = \text{C}_{1-3}$  alkyl as external donors. The effect of the external alkoxy silane donor on the polymerization strongly depended on the number and size of alkoxy groups and the size of hydrocarbon groups attached to the silicon atom. Two major effects were observed : selective deactivation of atactic active centers and the increased production of high-molecular-weight isotactic polypropylene. Evidently, at least on free non-hindered alkoxy group in the complex between alkoxy silane and  $\text{AlEt}_3$  is required for the selective deactivation.



Kokta and Raj [30] correlated the interaction occurring between the catalytic components of a Ziegler-Natta stereospecific system formed by  $\text{TiCl}_3$  and  $\text{AlEt}_3$  in heptane and the polymerization process. Titanium trichloride was prepared by the reduction of titanium tetrachloride with hydrogen on tungsten spiral. The addition of electron donor (e.g. pyridine) to the catalyst system formed by non-activated  $\text{TiCl}_3$  and  $\text{AlEt}_3$  can either increase or inhibit the rate of polymerization.

Kokta and Raj [31] had clarified that the formation and decay of the active centers are independent. The interaction of the catalyst components, influences the rate of polymerization. They also showed later that the rate of propylene polymerization is influenced by the rate of the interaction, activation energy, and the efficiency of interaction [32].

Tasuya Miyatake et al. [33] studied the effect of phenyltrimethoxysilane (PTMS) as an external electron donor on the microtacticity distribution of the isotactic parts of polypropylene prepared with  $\text{MgCl}_2$ -supported Ti catalyst- $\text{AlEt}_3$  system by programmed temperature column fractionation (PTCF) technique. PTMS deactivated nonstereospecific and low isospecific sites and enhanced stereoregulating ability of highly isospecific sites.

Sacchi [34] used  $^{13}\text{C}$  NMR to study the effect of the Lewis base on high yield supported Ziegler-Natta catalysts for isotactic propylene polymerization. They found that the role of the internal base are as follows:

(i) The base,  $\text{MgCl}_2$  and  $\text{TiCl}_4$  formed a three-component complex, which was the real active center; thus the base had a direct function to catalyze.

(ii) The two-component complex  $\text{MgCl}_2\text{-TiCl}_4$  was the true polymerization center; thus, the base had an indirect function, for instance, of controlling the titanium fixation on  $\text{MgCl}_2$ .

Coutinho and Santa Maria [35] studied the effect of di-n-butyl ether (DBE) in the synthesis of a highly active propylene polymerization catalyst. Electron-donors having ester and phosphate groups (ethyl benzoate-EB, diisobutyl phthalate-DIBP, tri-n-butyl phosphate-TBP) were added as second internal bases ( $\text{IB}_2$ ) in the catalysts prepared by the reduction of  $\text{TiCl}_4$  with  $\text{AlClEt}_2$  (DEAC) in the presence of DBE as a first internal base ( $\text{IB}_1$ ). The crystalline forms were examined for all catalyst samples by X-ray method.  $\beta\text{-TiCl}_3$  is brown with a fiber-shaped structure.  $\alpha$ -,  $\gamma$ - and  $\delta\text{-TiCl}_3$  are violet with a lamellar structure. The catalyst system based on the  $\beta$ -modification of  $\text{TiCl}_3$  and organoaluminium compounds exhibited low stereospecificity and activity in the propylene polymerization. The violet modifications based on  $\text{TiCl}_3$ , specially the  $\delta$ -

modification, produced highly active and highly stereospecific catalyst systems for propylene polymerization.

Yang and Hsu [36] studied the effects of four different external Lewis bases namely ethylbenzoate (EB), dimethoxydiphenyl silane (DMDPS), 2,2,6,6-tetramethylpiperidine (TMPip) and t-butylmethylether (TBME) on propylene polymerization using the  $MgCl_2$  - supported  $TiCl_4$  catalyst. The internal Lewis base used in this study was dioctylphthalate (POC). With ethyl benzoate as the external donor no change in activity was observed, but the interaction between ethyl benzoate and  $MgCl_2$ -phthaloyl chloride complex resulted in a decrease of isotacticity. Increasing the bulkiness of the external Lewis base hindered the monomer coordination. It was found that the relative amount of the phthaloyl chloride complex to other complexes played an important role in the formation of active sites.